INVESTIGATIONS FOR DENDRITE SUPPRESSION IN LITHIUM AND SODIUM METAL BATTERIES

A thesis presented for the award of the degree of

Doctor of Philosophy

from

University of Technology Sydney

By

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DEDICATION

This thesis is dedicated to my family.

CERTIFICATE OF ORIGINAL AUTHORSHIP

I, Kang Yan, declare that this thesis, is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Faculty of Science at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise reference or acknowledgement. In addition, I certify that all information sources and literature used are indicated in the thesis.

This document has not been submitted for qualifications at any other academic institution.

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Kang Yan

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STATEMENT OF FORMAT

This is the statement indicating that three published work are included in this thesis. Three original published work are referred to chapter 3, chapter 4 and chapter 5. The related publications in this thesis are listed as follows:

Title: Three-Dimensional Pie-Like Current Collectors for Dendrite-Free Lithium Metal Anodes. Authors: Kang Yan, Bing Sun, Paul Munroe, Guoxiu Wang. Journal: Energy Storage Materials, 2018, 11, 127-133. DOI: 10.1016/j.ensm.2017.10.012. This work is referred to chapter 3.

Title: Temperature-Dependent Nucleation and Growth of Dendrite-Free Lithium Metal Anodes. Authors: Kang Yan, Jiangyan Wang, Shuoqing Zhao, Dong Zhou, Bing Sun, Yi Cui, Guoxiu Wang. Journal: Angewandte Chemie International Edition, 2019, 58, 11364-11368. DOI: 10.1002/ange.201905251. This work is referred to chapter 4.

Title: Dendrite-Free Sodium Metal Batteries Enabled by the Release of Contact Strain on Flexible and Sodiophilic Matrix. Authors: Kang Yan, Shuoqing Zhao, Jinqiang Zhang, Javad Safaei, Xingxing Yu, Tianyi Wang, Shijian Wang, Bing Sun, Guoxiu Wang. Journal: Nano Letters, 2020. DOI: 10.1021/acs.nanolett.0c02215. This work is referred to chapter 5.

RESEARCH PUBLICATIONS

1. **Kang Yan**, Shuoqing Zhao, Jinqiang Zhang, Javad Safaei, Xingxing Yu, Tianyi Wang, Shijian Wang, Bing Sun, Guoxiu Wang, Dendrite-Free Sodium Metal Batteries Enabled by the Release of Contact Strain on Flexible and Sodiophilic Matrix, **Nano Letters**. 2020, DOI: 10.1021/acs.nanolett.0c02215.

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ABSTRACT

Lithium (Li) metal possesses very high specific capacity and low electrochemical potential, which shows great advantages to be used in next generation rechargeable Li metal batteries (LMBs). However, poor cyclability of Li metal anodes caused by inhomogeneous and uncontrolled Li deposition hinders the practical applications of rechargeable LMBs. Here, in order to effectively suppress Li dendrite growth without degrading the specific capacity, a three-dimensional (3D) pie-like current collector was prepared based on copper nanowires (CuNWs) and graphene (GE). The interior space of CuNWs framework efficiently accommodate Li deposition. Meanwhile, the GE layer wrapped outside CuNWs functions as flexible protective layer that could protect extra Li deposition. The CuNWs@GE current collectors demonstrated several merits to achieve better Li metal anodes with significantly improved Coulombic efficiency and cyclability for rechargeable LMBs.

It is essential to develop a facile and effective method to enhance the electrochemical performance of Li metal anodes for building high-energy-density LMBs. Herein, we explored the temperature-dependent Li nucleation and growth behavior and constructed a dendrite-free Li metal anode by elevating temperature from room temperature (20 ℃) to 60 ℃. A series of *ex situ* and *in situ* microscopy investigations demonstrate that increasing Li deposition temperature results in large nuclei size, low nucleation density, and compact growth of Li metal. We reveal that enhanced lithiophilicity and increased Li-ion diffusion coefficient in aprotic electrolytes at high temperature are essential factors contributing to the dendrite-free Li growth. As anodes in both half-cell and full-cell, the compact deposited Li

with minimized specific surface area delivered high Coulombic efficiencies and long cycling stability at 60 ℃.

The formation of sodium (Na) dendrites during cycling has impeded the practical application of Na metal anodes. Herein, we developed a flexible graphene-based matrix, *e.g.*, porous reduced graphene oxide (PRGO) film, to support dendrite-free Na nucleation and plating, contributing to high-performance Na metal batteries. The PRGO film possessed outstanding merits of sodiophilicity and flexibility. The sodiophilic PRGO film enabled uniform Na nucleation. Furthermore, the flexible PRGO film alleviated the texture deformation of electrodeposited Na, leading to a compact and dendrite-free Na deposition layer. The well-maintained Na metal anodes on PRGO films exhibited superior cyclability, high Coulombic efficiency, and improved energy density in both half-cell and full-cell testing. This work illustrates the great significance of mechanical properties of the supporting matrix for the Na electroplating, which provides a new strategy to develop high-performance dendrite-free Na metal batteries.